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Effect of incorporation manner of Zr on the Co/SBA-15 catalyst for the Fischer–Tropsch synthesis

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ABSTRACT

The effect of incorporation manner of Zr on the textural properties, surface physicochemical properties, reduction degree and catalytic performance of Co/SBA-15 catalyst for the Fischer–Tropsch synthesis (FTS) was investigated. The catalysts were prepared by sequential impregnation, co-impregnation and in-situ synthesis method, respectively. The loading amount of Co and Zr remained constant in all catalysts with 15 wt.% and 5 wt.%, respectively. The catalysts were characterized by N_2 adsorption–desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), temperature-programmed reduction (H_2-TPR) and evaluated for the FTS. It was revealed that the Co_3O_4 was considered as the main surface cobalt phase, and the BET surface area and pore size were decreased regardless of the incorporation manner. The reduction degree of cobalt species increased from 80% (Co/SBA-15) to 90% (Co/Zr/SBA-15) and 85% (CoZr/SBA-15) with the addition of Zr, except for the Co/Zr-SBA-15 catalyst (74%). The catalyst prepared by sequential impregnation method (Co/Zr/SBA-15) showed the highest selectivity of long-chain hydrocarbons (C_{12}–C_{22}, 53%) with the chain growth probability α up to 0.84, which could be attributed to the highest reducibility of cobalt species.

1. Introduction

The Fischer–Tropsch synthesis (FTS) is a process that converts a mixture of carbon monoxide and hydrogen (also known as syngas) into clean liquid fuels or valuable chemicals [1,2]. Compared with the refinery diesel, the predominantly linear paraffinic hydrocarbons along with virtually no contaminants such as sulphur, nitrogen and aromatics in the FTS show a higher cetane number and lower pollutant emission level [2]. FTS has sparked renewed interest in utilization of nonpetroleum carbon resources (such as natural gas, coal and biomass) in recent years because of the increasingly stringent environmental regulations and the depletion of light and sweet petroleum reserves.

Extensive researches on the FTS catalysts based on Ru, Co and Fe have been reported [1,3–5]. The high cost and low availability of Ru-based catalysts are important concerns limiting their commercial application. Compared to Fe-based catalyst, Co-based catalysts for FTS are usually preferred under carefully selected temperature and H_2/CO ratio, and show higher selectivity in linear long-chain paraffin fractions, slower deactivation by water (a by-product of the FTS reaction), less oxygenates and lower CO_2 selectivity [6–8]. Thus, the Co-based catalysts have attracted much attention for the synthesis of wax and liquid-fuel, while the Fe-based catalysts are suitable for the production of alkenes and oxygenate chemicals. Generally, the products of FTS follow the Anderson–Schultz–Flory (ASF) distribution due to the polymerization mechanism. Thus, the liquid fuels (mainly gasoline and diesel fuel) are usually obtained by the catalytic cracking process after FTS [9,10]. Recently, several studies have succeeded in the direct production of middle isoparaffins (C_5–C_{12}) or C_{10}–C_{20} hydrocarbons with high selectivity [1,11,12].

It is generally accepted that the activity of Co-based catalysts for FTS is proportional to the density of surface active Co^0. Therefore, Co species should be both highly dispersed and reduced on the catalyst surface [2,11]. For this reason, Co is commonly deposited on high surface area supports such as SiO_2, Al_2O_3 and TiO_2, probably the most extensively used for Co-based FTS catalysts. In the last decades, other alternative supports with mesoporous silicas have also been explored to provide new possibilities for tuning the products selectivity [13,14]. In particular, the SBA-15 with high surface area and narrow pore diameter distribution allows for high Co dispersion even at high metal loadings and can realize spatial confinement on the metal particle size to restrict the

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formation of hydrocarbons longer than some characteristic size (say, carbon number $n < 20$) [9]. The addition of promoters, such as noble metals (Ru, Re) [8,15,16], transition metal oxides (ZrO_2 and MnO_x) [3,17,18] and some rare earth metal oxides (CaO, La_2O_3) [18,19] are capable of modifying the catalyst structure and improving the catalytic performance by enhancing the dispersion and reduction degree of cobalt species. A number of investigations have been focused on Zr-promoted Co catalysts, which exhibited higher CO conversion and C_{5+} selectivity for FTS than the un-promoted catalysts. Ali et al. [20] reported that the weaker Co–Zr interaction created an active interface that increased activity by favoring CO dissociation. Andreas and Moradi et al. [21,22] ascribed the increased activity to the easy reduction of cobalt species with the addition of Zr. Rohr et al. [23] concluded that the addition of ZrO_2 to Co/Al_2O_3 catalyst increased the activity and selectivity to heavy hydrocarbons, while reducibility and dispersion have not been improved. Therefore, it is necessary to clarify the influence of Zr on the catalysts textural properties, surface physicochemical properties, reduction degree and catalytic performance for FTS reaction.

In the present contribution, the 15 wt.% Co/SBA-15 catalysts with 5 wt.% Zr promotion were prepared in three different manners to provide the insight into the Zr modification on properties and product distributions of the catalysts. These catalysts were characterized by means of N_2 adsorption–desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) as well as temperature programmed reduction (H_2-TPR) to elucidate the Co–Zr interaction, dispersion and reducibility of Co species. And the catalytic performances of the catalysts were tested in FTS by using a fixed bed reactor.

2. Experimental

2.1. Catalyst preparation

The detailed preparation of SBA-15 can be found in elsewhere [9]. Co/SBA-15 catalyst was prepared by incipient wet impregnation of the SBA-15 support with a desired amount of cobalt(II) nitrate dissolved in water in equal with respect to the pore volume of the SBA-15 support. The precursor were dried at 120 °C and calcined at 400 °C for 4 h. The loading amount of Co in the final catalyst was 15 wt.%.

Co/Zr/SBA-15 was prepared by sequentially impregnated method. Typically, the SBA-15 support was firstly impregnated with a desired amount of aqueous zirconium (IV) nitrate. After dried at 120 °C and calcined at 400 °C for 4 h, the Zr/SBA-15 was obtained. Then it was impregnated with the aqueous of cobalt(II) nitrate followed by drying at 120 °C and calcination at 400 °C for 4 h. The loading amount of Zr and Co in the final catalyst was 5 wt.% and 15 wt.%, respectively, which were reported by Mu et al. for the maximum CO conversion and C_{5+} selectivity in the FTS [24].

CoZr/SBA-15 was prepared by co-impregnated method. The SBA-15 support was impregnated with a desired amount of zirconium(IV) nitrate and cobalt(II) nitrate dissolved in water in equal with respect to the pore volume of the SBA-15 support. Then it was dried at 120 °C and calcined at 400 °C for 4 h. The loading amount of Zr and Co in the final catalysts was the same as Co/Zr/SBA-15.

Zr-SBA-15 was synthesized in-situ as follows: P123 (EO20PO70EO20, MAV = 5800, Aldrich) was dissolved in 2 M HCl with stirring to obtain a clear solution. TEOS (Aldrich) and $ZrOCl_2{\cdot}8H_2O$ were gradually added into the solution with continuous stirring for 24 h. The mixture was hydrothermally treated to crystallize in a Teflon-lined autoclave at 120 °C for 24 h followed by filtering, washing and drying at 120 °C. Calcination of the dried cake was then carried out in an electric oven in air at 400 °C for 6 h. Finally, the Co/Zr-SBA-15 was prepared by incipient wet impregnation method as the same preparation procedure of Co/SBA-15. The loading amount of Zr and Co was the same as Co/Zr/SBA-15.

All the chemicals were supplied by Sinopharm Chemical Reagent Co., Ltd. China and used as received.

2.2. Catalyst characterization

Nitrogen adsorption–desorption were measured on an ASAP 2010 Micromeritics to determine the BET surface area and porosity. Prior to the measurements, the samples were degassed at 300 °C for 5 h. Nitrogen isotherms were obtained in both adsorption and desorption modes. The surface area was determined by the BET method and the pore volume was calculated from the amount of vapor adsorbed at a relative pressure of 0.995. Pore size were established from the desorption branches of the isotherms using the Barret-Joyner-Halender (BJH) method [13].

X-ray diffraction patterns of the catalysts were collected on a Brukers D8 powder diffractometer with Cu-Kα radiation at a rate of $4^\circ\,min^{-1}$ in the range $2\theta = 0^\circ–70^\circ$. The average crystallite size of Co_3O_4 ($d(Co_3O_4)$) was calculated from the Scherrer equation $d(Co_3O_4) = K\lambda/T\cos\theta$ at the most intense reflexion $2\theta = 36.9^\circ$ [25,26], where K is a constant near unity, and T is the average thickness of the crystal. The Co_3O_4 crystallite sizes in the samples were then converted to the corresponding cobalt metal diameters in reduced catalyst using the equation: $d(Co^0) = 0.75 \times d(Co_3O_4)$ [27]. The Co^0 metal dispersions could be calculated using $D = 96/d(Co^0)$, assuming a spherical geometry of the metal particles with uniform site density of 14.6 $atoms/nm^2$, Where D is the% dispersion and d is the average crystallite size of Co^0 in nm [1].

The X-ray photoelectron spectroscopy (XPS) was performed on a Physical Electronics Company Quantum-2000 Scaning ESCA Microprobe spectrometer. The Al-Kα non-monochromatized line (1486.6 eV) of a twin anode in the constant analyzer energy mode with a pass energy of 50 eV was used. In order to remove charging shifts and deal with Fermi edge coupling problems, the C 1s (284.6 eV) were used to revise all the binding energies (BEs).

The morphology of the catalyst samples was measured using scanning electron microscopy (SEM) with a Hitachi S-4800 microscope operated at 10 kV. Transmission electron microscopy (TEM) measurements were performed on a H-7650 electron microscope operated at an acceleration voltage of 100 kV.

The reduction behaviour of the samples was performed by temperature-programmed reduction (H_2-TPR) in a U-tube quartz cell. Firstly, about 100 mg of the calcined catalyst was purged with Ar (40 $mL\,min^{-1}$) at 300 °C for 1 h and cooled to 50 °C. After that, it was exposed to 10 vol% H_2/Ar (40 $mL\,min^{-1}$) with the temperature from 100 °C to 800 °C at a ramp rate of 10 °C min^{-1}. A different set of experiments was performed in the same equipment to determine the reduction degree of cobalt oxides. About 100 mg of calcined catalyst was loaded into the U-tube quartz cell and reduced in-situ at 450 °C for 6 h at a heating rate of 1 °C min^{-1} in the 10 vol% H_2/Ar (40 $mL\,min^{-1}$). The H_2 consumption amount was monitored with a thermal conductivity detector (TCD) and corrected by the CuO reduction. The reduction degree was calculated on the amount of H_2 consumed during the reduction treatment at 450 °C divided by stoichiometric amounts of H_2 required for the complete reduction of cobalt oxides.

2.3. Catalytic performance test

The FTS reaction was performed in a pressured fixed-bed reactor (d_{int} = 8 mm, l = 40 cm) at 2 MPa, 240 °C and space velocity (GHSV) of 1000 h^{-1}. Typically, a catalyst of ∼1.5 mL was mixed with 1.5 mL of quartz particles and charged into the reactor to form a diluted catalyst bed. The catalyst was initially reduced at 450 °C for 6 h in a H_2